

Manipulating the crystallization kinetics and morphology of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ via addition of citrate at high levels of supersaturation and the effect of high salinity

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ABSTRACT

Citrate ion possesses the right structure to be strongly bound on specific crystal faces of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, which results in an increase in the induction time of precipitation, and changes the structure and morphology of the solid. The inhibition of the precipitation kinetics of gypsum, in the stoichiometric reaction of Na_2SO_4 and CaCl_2 was investigated in aqueous solutions with high supersaturation (0.1 M initial reactant concentrations). The induction time was found to be the longest when the inhibitor was present in fully deprotonated form in the solution ($\text{pH} > 5$). The inhibition effect levels off with the increasing inhibitor concentrations (ca. 3 mM). As a result of citrate binding, on the basis of SEM measurements, the morphology of the crystals change from rod-like to plate-like. Addition of high concentration of NaCl (mimicking seawater conditions) was found to facilitate the inhibition, but from the morphological studies, the inhibition mechanism of citrate appears to change under hypersaline conditions (relative to systems without added electrolyte.) From UV and IR spectroscopic measurements, it was found that the inhibitor ended up in the mother liquor after the completion of the precipitation reaction.

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1. Introduction

Additives of various kinds have been frequently used to manipulate the crystallization process of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Even in the first reports published in this field in 1958, the possibility of inhibiting crystallization reaction with using different additives was already discussed [1,2], and it was suggested that the most adequate types of inhibitors were the ones which were capable of binding onto the surface of the crystals forming, thus altering the growth process of the crystals. Organic compounds with functional groups capable of forming complexes with calcium in solution may be able to act in the same (or similar) way on the crystal surface. Up until today, it is understandably a popular and

widely investigated topic considering the associated problems found in several industrial processes.

Over the years, phosphonates and carboxylate-containing polymers yielded the most remarkable results, but many other potentially useful compounds were also identified. Phosphonate groups can be strongly bound to calcium, they are commercially available and are often used as antiscalants [3]. Several studies prove that they are potent inhibitors, even in small concentrations [4–9]. It was suggested that two phosphonate groups can coordinate to a single calcium atom, replacing the water molecules or if the structures allow it, different phosphonate groups can bind to neighboring calcium atoms forming chelate-like surface complexes [8]. Since these additives also affect the crystallization through surface interactions, it is expected that they can alter the morphology of the precipitating crystals. It was found that at elevated temperature and in acidic media, they were still capable of slowing down the process [10]. Comparing their effectiveness to other organic additives utilized in this reaction, the phosphonates are usually “top-performing” inhibitors [8,11]; however, if they are used in

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large amounts, they are considered to be environmentally “unfriendly”, therefore if possible, they are avoided in large-scale applications.

One alternative for phosphorous-free additives are polycarboxylates. They were found to be potent inhibitors for gypsum precipitation [2]. Their performance can be improved by adjusting the pH of the reaction mixture to the experimentally found optimal value or by building other functional groups (for example hydroxyl and amino groups) into their structure to facilitate surface bonding [12]. Among others, poly(acrylic acid) and poly(-maleic acid), were applied successfully as inhibitors [12–19]. Because of the surface interaction between these additives and gypsum, they are also capable of modifying the morphology of the crystals. Since gypsum is an undesirable precipitant in various processes, inhibitors need to work under diverse conditions. Polycarboxylates were tested successfully under close-to-standard circumstances [12,13], at elevated temperature [14], in acidic media [17], in industrial water models [16] and retarded scaling on heated surfaces [15] proving their usefulness in many aspects. However, just like phosphorous-containing antiscalants, some of these polymers represent considerable environmental risk, therefore their use is restricted, being non-biodegradable, e.g., poly(acrylic acid). In recent years some “green”, biodegradable polymers were tested instead, as potential substitutes in water treatment during scale inhibition [18,19]. The efficiency of these polymers is varied, some of them (e.g., poly(aspartic acid) and poly(epoxysuccinic acid)) performed well during the test experiments.

The inhibiting efficacy of the above additive groups of compounds is outstanding, but they are not the only ones applied. Some macromolecules, bovine serum albumin, humic acid and sodium alginate were able to suppress the bulk crystallization of gypsum, but in reverse osmosis experiments, they enhanced surface nucleation decreasing membrane permeability [20]. The addition of surfactant has varied effects. The addition of cetyltrimethylammonium bromide (CTAB), a cationic and surfactant, seems to decrease the nucleation time and enhance the growth rate, while sodium dodecyl sulfate (SDS), an anionic one, has opposite effects, it increased the nucleation time and decreased growth rate [21]. Some amino acids were found to be effective in delaying the growth of gypsum in seeded experiments with low supersaturation [22].

As polycarboxylates are very efficient inhibitors in gypsum precipitation, it is logical to assume that small molecular weight di- or tricarboxylic acids may also have this effect. A number of them were tested as additives with varying success, but it is certain that citric acid stands out from them [23–25]. Citric acid became a popular additive in gypsum crystallization for multiple reasons. As mentioned above, its efficiency is much higher than that of other carboxylic acids. It is present in nature, and is part of natural biological processes, therefore it does not present an environmental threat; it is truly a “green” organic. These reasons, and in addition to this, its moderate price makes citric acid a promising candidate for inhibiting calcium sulfate crystallization during various processes.

Studies on the nucleation kinetics of gypsum in the presence of small amounts of citric acid showed that it could increase the induction time of the reaction. Experiments carried out with using slightly varying temperature, additive concentration and moderate supersaturations made it possible to calculate the variations in the interfacial tension between gypsum crystal and the aqueous solution [26,27]. The presence of citric acid affects the morphology of the crystals forming. The extent of this effect depends on the experimental parameters employed and the concentration of the additive [28–30]. If their individual contributions are determined, the information can be useful for various

processes, because with varying morphology and crystal size the filtering properties of the solid change. This parameter is critical for example in the wet process of phosphoric acid production [31] and wet flue gas desulfurization process [32]. The effects of citric acid can also be utilized in the construction industry. The retarded settling time of gypsum provides more time for shaping the plaster, but can also decrease its compressive strength [33,34]; it can prohibit the pre-curing of gypsum during gypsum particle board manufacturing [35]. It is also a moderately effective scaling inhibitor in pipes at elevated temperatures [36].

The inhibition effect can be partly explained by the complex formation of citric acid and calcium ions, hence decreasing the supersaturation of the solution. However, this effect is not sufficient to achieve the observed efficiency in the inhibition of the precipitation, as Ca^{2+} and SO_4^{2-} are present in vast amounts compared to citrate [24,30]. Citrate interacts with the surface of the gypsum crystals, which could be a viable explanation for its inhibiting performance. Molecular modelling was used to calculate the distances between the carboxylic moieties of citric acid (3.5 Å), and was compared to the shortest Ca^{2+} - Ca^{2+} distance (3.7 Å) of the (1 1 1) crystal face of gypsum, which suggests that the formation of preferential (stable) surface complex comprising two surface metal ions and two carboxylate moieties of the same citrate ion is possible [37,38]. Similar results were found later complementing the initial findings and claiming that the closest Ca^{2+} - Ca^{2+} distance on the (120) plane makes it another preferable adsorption face [23,33]. A recent study using molecular dynamics simulation appeared to prove that the affinity of citrate compared to L-(+)-tartaric acid for binding on the surface of gypsum is higher, which explains the differences between their inhibiting effects [39]. Considering also that the (1 1 1) plane seems to be the fastest growing one of gypsum in aqueous system [30,40], it can be said that the outstanding inhibiting performance of citrate ion was a result of its high surface complex forming affinity on the most rapidly growing sites of gypsum.

In spite of the relatively large number of published works available in this field, there are still some uncovered areas regarding the feasibility of its use. It is mentioned that pH can affect its inhibiting potential [29,37], but (rather surprisingly) detailed investigation on this issue is still missing. The published works are aimed at systems with low supersaturation. The detailed study on the variation in the additive concentration also lacks. Its efficiency in solutions with high ionic strength needs some attention, which data could be useful for processes like desalination or heat exchange using geothermal waters. Since in these media, the regularly used conductometry is ineffective, the search for other applicable measuring method appears to be also of importance. Accordingly, we embarked on studying the crystallization kinetics of gypsum in the presence of citric acid/citrate with the aim of contributing to the description of these missing points listed above.

2. Experimental

2.1. Materials

Unless otherwise stated, the materials listed here were utilized without further purification or treatment.

The chemicals used were analytical grade products of VWR Hungary (anhydrous sodium sulfate, Na_2SO_4 ; calcium chloride dehydrate, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; sodium chloride, NaCl; trisodium citrate dehydrate, $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$; citric acid, $\text{C}_6\text{H}_8\text{O}_7$) and Sigma-Aldrich (now Merck) (sodium hydroxide, NaOH). The distilled water was obtained from a Millipore-MilliQ system.

2.2. Measuring equipment and methods

Variation of the electrical conductivity during the precipitation reactions were monitored using a Jenway 027013 conductivity cell connected to a Jenway 3540 pH and conductivity meter. The built-in sensor of the cell was also used to monitor the temperature.

The pH of the solutions was measured with a Sentix 62 pH electrode calibrated to 5 points at pH 2, 4, 7, 10, 11.5, using standard buffers.

The potentiometric measurements were carried out with a Metrohm 794 Basic Titrino equipped with a Metrohm combined polymer membrane Ca ion-selective electrode (Ca-ISE).

For the powder X-ray diffractometric measurements, a Rigaku MiniFlex II type Röntgen diffractometer was used. The diffractograms of the precipitates were captured in the

$2\theta = 4^\circ\text{--}60^\circ$ range with $2^\circ/\text{min}$ scanning speed, using $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation.

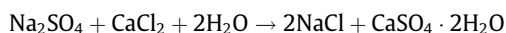
The morphologies of the precipitated solids were studied by scanning electron microscopy using a Hitachi S-4700 scanning electron microscope. This instrument was also equipped with a Röntec QX2 spectrometer enabling the elemental mapping of the solids.

UV–Vis spectra of the solutions were measured by an Analytic Jena Specord 210 plus spectrophotometer, using a quartz cuvette.

IR spectra of the solids was measured on a BIO-RAD 18 Digilab Division FTS-65 A/896 FT-IR spectrophotometer using the DRS technique and collecting 256 interferograms for one spectrum, with resolution of 4 cm^{-1} . KBr was used for background.

2.3. Experimental procedures

To study the kinetics of the precipitation reaction of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the following reaction was carried out:



The details of the setup and the comprehensive kinetic model obtained from the measurements in systems free from any inhibitor were described in our previous work [41]. In brief, $50\text{--}50 \text{ cm}^3$ solutions were prepared containing stoichiometric amounts of reactants, and they were mixed to initiate the reaction. These solutions were made of analytical grade solids with exact mass measurements using an analytical balance. To exclude the inaccuracy caused by the uptake of moisture, the solids were kept at 100°C for 12 h. The measurements were carried out in a smooth surfaced, spherical PTFE vessel, which was thermostated at 25°C , in every reaction.

For good repeatability the strict control of the reaction conditions is needed, therefore every parameter which were able to influence the kinetics were kept constant (as much as it was possible). The same vessel and stirring equipment was used in every reaction. The agitation was performed with a magnetic stirrer with adjustable agitation rate, always using the same stirring rod. To minimize the changes in the reactions hydrodynamics, even the electrodes were used in the same positions.

The reactions were monitored *in situ* either with conductometric or with potentiometric measurements using Ca-ISE for the latter. We have shown earlier [41] that for our systems conductometry is a suitable method even for fast reactions, but only in the absence of supporting electrolyte; on the contrary, Ca-ISE works well in, e.g., hypersaline solutions, but the precipitation reaction needs to be slow enough for the establishment of reliable potential readings. The reliability regions of these two *in situ* methods was checked with ICP-OES measurements, the results of which were published elsewhere [41].

To test the limitations of citric acid as an inhibitor, reaction conditions that favour the quick precipitation of gypsum were chosen.

The initial reactant concentration was chosen to be 0.1 M, the stirring rate 300 rpm (magnetic stirring). The pH of the reactions was adjusted using sodium hydroxide when it was needed. The additive was always dissolved in the sodium sulfate solution. The pH of the reactions was monitored during the individual runs using a calibrated pH electrode, while the kinetics were followed by *in situ* conductometric and in some cases potentiometric measurements, using Ca-ISE for the latter.

To investigate the effect of pH on the crystallization rate, it was systematically varied between 3.15 (the pH of the reaction mixture when citric acid is used as additive) and 10.

According to the results obtained, in the reactions to follow, trisodium citrate was used, ensuring that the carboxylate groups of the additive are largely deprotonated during the reactions. (We would like to note that we obtained $\text{pH} \sim 6.5$ for Na-citrate solutions, which is most probably due to some citric acid traces in the solid or, less probably, to some airborne CO_2 .) The additive concentration was systematically increased in the reaction mixture, until the inhibition effect did not change significantly with the increasing additive concentration.

After the reactions reached their equilibrium, the precipitates were separated with vacuum filtration through filtering paper with $0.45 \mu\text{m}$ pore diameter without washing any of the samples. The solids were then dried at 60°C for 12 h. The structure and composition of the samples were investigated by powder XRD. The morphologies of the solids were also studied by capturing their SEM images.

To determine if the additive was incorporated in the precipitating solids, the filtrate and the precipitate were both studied. The fluids were analyzed by UV spectrophotometry and the solids by IR spectroscopy, since both measuring methods are capable of detecting carboxylate groups in the samples.

The effect of citric acid was also investigated in solutions with high ionic strength. In these experiments, the stoichiometric reaction of Na_2SO_4 and CaCl_2 was carried out with 0.1 M initial reactant concentration, in the presence of 1 M NaCl background electrolyte (which increased to 1.2 M by the end of the reaction, from including the NaCl stemming from the reactants) to imitate conditions similar to those present in seawater. The agitation rate was 300 rpm, and the concentration of additive (citric acid and trisodium citrate) was 1.5 mM. As the conductivity of the background electrolyte was very high compared to the effect of the precipitation reaction, instead of conductometry, the reactions were followed by direct potentiometry using Ca-ISE with two-point calibration (initial and final Ca^{2+} concentration).

At the end of the reactions, the solids were filtered, their compositions were determined by powder XRD and the morphologies were investigated by capturing the SEM images of the solid samples, to compare the effect of the inhibitor in the absence and in the presence of background electrolytes.

3. Results and discussion

Citric acid is an efficient crystallization inhibitor in general and in gypsum precipitation in particular [26–40]. In close-to-industrial conditions and at high gypsum supersaturation, the inhibiting effect of citric acid is still largely unexplored, therefore our test reactions were performed under conditions, where the gypsum precipitation is favored in inhibitor-free systems.

While the pH has generally no effect on the solubility and hence on the kinetics of the precipitation of gypsum, it still can influence the applied inhibitor. As the citric acid interacts with the crystal surfaces by coordinating to the available calcium ions through its carboxylate groups, the protonation and deprotonation of these groups can alter the result of the inhibition. This was mentioned

earlier [38], but usually receives little attention in the literature. To investigate this in detail, the stoichiometric reaction of Na_2SO_4 and CaCl_2 was carried out in the presence of 1.5 mM citric acid adjusting the reaction pH with NaOH. The pH of the systems did not vary significantly during the precipitation reactions; the maximal variation was within 0.1 pH unit. The induction times (defined as the time elapsed from starting the reaction until the conductance or in the later experiments the Ca-ISE electrode potential variation exceeded the natural fluctuation of the electrode signal) corresponding to the different solution pH values are presented in Fig. 1.

The pH of the reaction was varied systematically between 3.15 (adding citric acid without further adjustment of pH) and 10. The 6.5 value was achieved by using trisodium citrate without further adjustment of the pH. It can be seen that under pH 5 the reaction is induced faster, the inhibiting efficiency of citric acid is decreasing rapidly especially under pH 4. The induction time obtained for the reaction around pH 3 was approximately 6.5 min, which is still significantly longer, than the *c.a.* 1.7 min observed in the absence of the additive. The decrease in inhibiting efficiency is expected, since the protonation of the carboxylic groups of citric acid takes place in this region [42]. This process should only affect the reaction mainly under pH 6; however, it is not the case. The interaction of the additive with calcium ions can affect the process as the metal ions replace the protons by bonding with the ligand forming complexes. The calcium-citrate complexes are dissociated below pH 4 (pK_c of calcium citrate is 3.38 [43]), which explains the sharp drop of induction time under this pH value. To illustrate this, on Fig. 2 two distribution diagrams are presented, the protonation of citric acid and its complexation in the presence of calcium under our experimental circumstances. Above pH 5, the reaction kinetics did not change significantly with the increasing pH.

The pH of the reactions is close to neutral when trisodium citrate is used as an inhibitor, therefore in the following reactions this form of the additive was used. To investigate the concentration dependence of citrate inhibition, gypsum was precipitated in the stoichiometric reaction of Na_2SO_4 and CaCl_2 , with 0.1 M initial reactant concentration systematically increasing the concentration of added trisodium citrate, until the inhibiting effect did not increase further with the increased additive amount. The results of these measurements are shown in Fig. 3.

It can be seen that even small amounts of citrate ions increase the induction time significantly, and the effect increases systematically but not proportionally with the increasing additive concen-

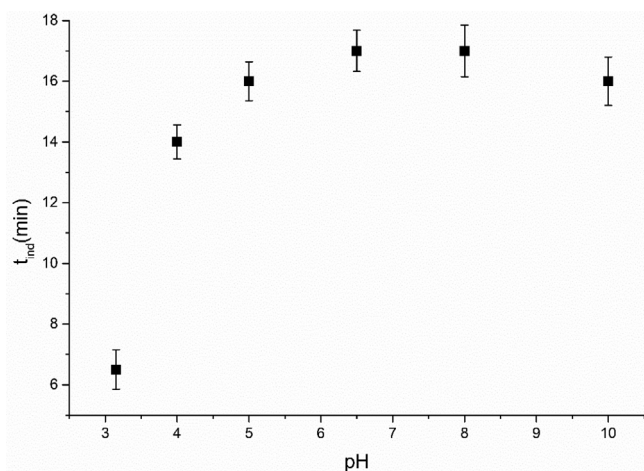


Fig. 1. The effect of pH on the inhibiting efficiency of citric acid in the precipitation reaction of gypsum ($\text{CaCl}_2 + \text{Na}_2\text{SO}_4 + 2 \text{H}_2\text{O} \rightarrow 2 \text{NaCl} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with 0.1 M initial reactant concentration, in the presence of 1.5 mM citric acid, average of three parallel measurements).

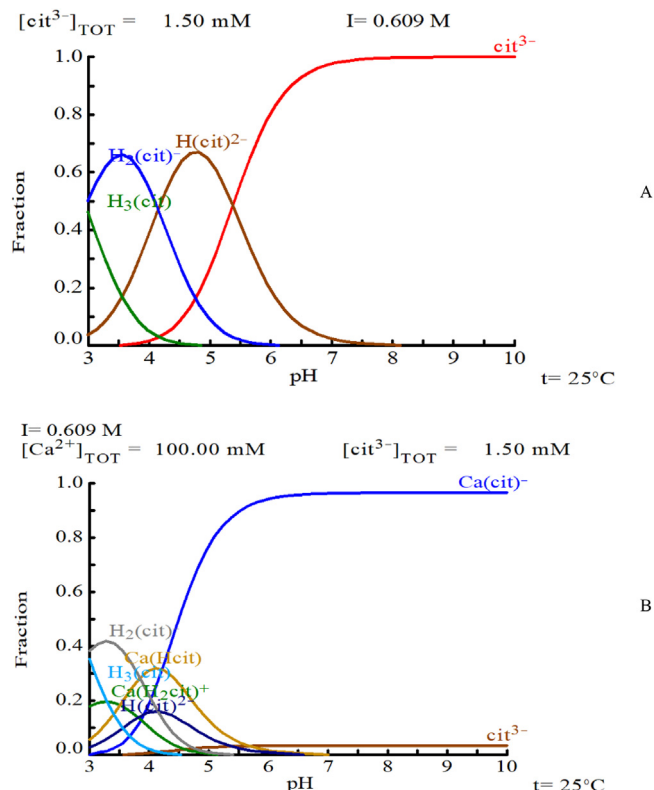


Fig. 2. Distribution diagrams of A: citric acid protonation in absence of calcium and B: its complexation and protonation in the presence of calcium. The diagrams were created by Medusa/Hydra software and database (input parameters similar to precipitation reaction conditions: 0.1 M initial reactant concentration, 1.5 mM citric acid at 25 °C).

tration: above 3 mM there are only marginal variations in the induction time and crystal growth process. This can be explained in terms of the inhibition mechanism of the citrate ions. The concentration of citrate (1.5 mM) is only a fraction of the calcium-ions (100 mM) present in the solution, therefore the formation of complexes is not expected to affect the reaction significantly. For stable crystals to form and be able to grow, the components have to aggregate to reach the critical nucleus size. Before they reach this size, they more readily dissolve than grow. In recent studies it was shown that in the first step of gypsum precipitation, preliminary phases are formed, which are later reorganize to form the gypsum crystals [44,45]. As citrate is a relatively small molecule, it could bound to the surfaces of the particles below critical size, and when these surfaces become saturated, the nucleation time does not increase any further. In a recent study Nicoleau et al. [46] showed that some polymers can bound to the surface of these preliminary faces, retarding the nucleation and crystal growth of gypsum. Similarly, bounding on the crystal surfaces citrate can slow down both the nucleation and the crystal growth processes of gypsum. As the citrate ions are coordinated only to a few crystal surfaces, where the arrangement of the calcium ions are optimal, complete inhibition of the reaction is not possible; however, the observed relatively long induction times are promising for practical applications.

After the reactions reached their equilibrium, the solids were separated using vacuum filtration, and their composition was determined by powder XRD, the results can be seen in Fig. 4.

It can be seen that the addition of citric acid has major effect on the intensity of some of the reflections of the gypsum crystals obtained as well as on the ratio of the individual reflections within

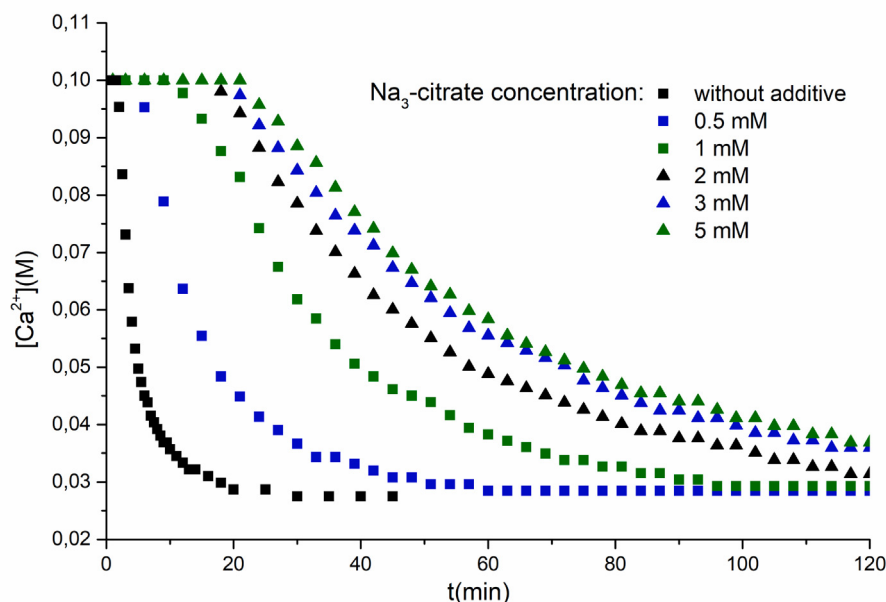


Fig. 3. Variation of $[\text{Ca}^{2+}]$ (calculated from the results of conductometric measurements) during the stoichiometric reaction of Na_2SO_4 and CaCl_2 , with 0.1 M reactant concentration systematically varying the concentration of added trisodium citrate.

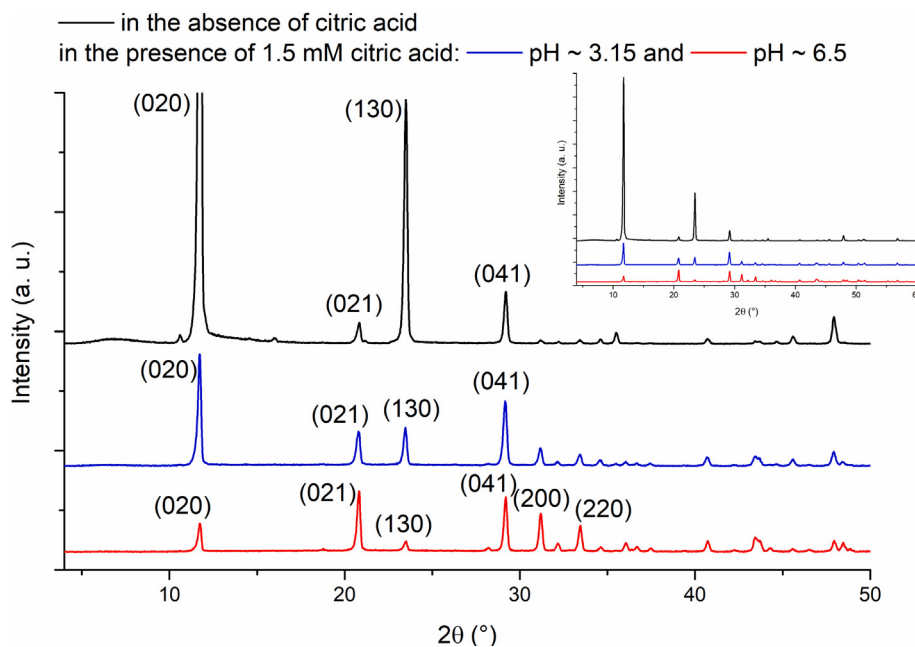


Fig. 4. XRD patterns of gypsum crystallized in the absence and in the presence of citric acid in different protonation forms, in the stoichiometric reaction of Na_2SO_4 and CaCl_2 , with 0.1 M reactant concentration (insert presents the same patterns without truncating the signal corresponding to the (020) reflection of gypsum precipitated in absence of additive) the Miller indices of the main reflections were identified with the help of the JCPDS database ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$: # 21-0816).

one sample. The most intense peaks decrease to the point where they are comparable or even smaller than the smallest reflections seen in the absence of additive. The intensity of the reflections corresponding to the crystal lattices with (0 2 0) and (1 3 0) Miller indices were significantly decreased when the reaction was carried out in the presence of citric acid (pH ~ 3) and they are even less intensive in presence of trisodium citrate (pH ~ 6.5).

These changes suggest that the morphology of the solid should be also changed, which is expected on the basis of literature data

[28–30], too. The changes were studied by recording the SEM images of the precipitate samples (Fig. 5).

It can be seen in Fig. 4 that in the absence of additive, the gypsum is precipitated as rod-like crystals. Precipitating them in the presence of citric acid at pH ~ 3, the morphology of the crystals remain the same. This confirms that the inhibitor with protonated donor groups is not able to interact with the crystal surfaces. However, as the pH is increased, the crystals tend to form platelets due to the retarded crystal growth rate on specific crystal faces, namely

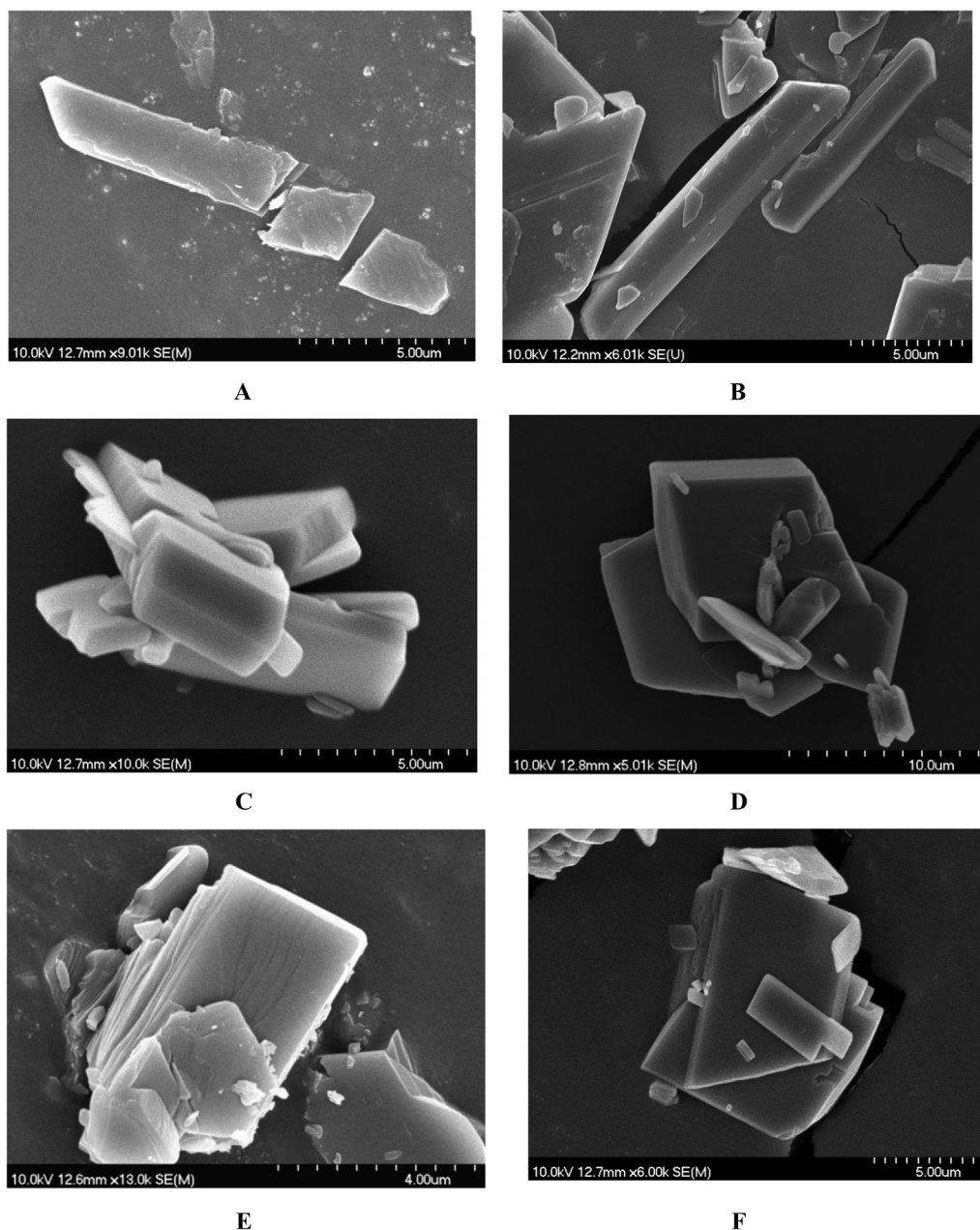


Fig. 5. SEM images of the solid samples precipitated in the stoichiometric reaction of Na_2SO_4 and CaCl_2 with 0.1 M reactant concentration A: in the absence of additive; B: in the presence of 1.5 mM citric acid (pH ~ 3); C: in presence of citric acid at pH 4 D: in presence of citric acid/trisodium citrate at pH 5; E: in presence of trisodium citrate at pH 6.5; F: in presence of trisodium citrate at pH 10.

on the (1 1 1) and (1 2 0) crystal faces. The crystals precipitated at pH 4 are similar to those obtained at pH 3, and the morphological transition becomes more pronounced at pH 5. The crystals forming at pH-s higher than this have practically identical morphology. This observation is in line with the data published in the literature [23,33,37,38]. On some of the SEM pictures it can be seen, that the crystals are broken, probably due to the relatively high agitation speed which causes the forming particles to collide with each other and the stirring rod more often.

The destination of the additive after the completion of the precipitation reaction is of importance for practical applications, since the potential reusability can affect the economic and environmental viabilities of the procedures. Though the incorporation of the additive in the crystals is unlikely, the fast precipitation of relatively high amount of crystals could result in the formation of some

inclusions. Furthermore, citrate ions could interact with the surface of the crystals, and thus remain on the solids after the reactions. The third option is that citrate remains in the mother liquor as free ligand or Ca complex.

To obtain more detailed insight, first, the filtrates of the reaction mixtures were studied by UV spectroscopy. Since the absorbance of the mother liquors was too high, they were diluted fivefold before the measurements. The spectra of filtrates from reactions with different amounts of citrate are compared with the filtrate from a blank reaction and with the 0.5 mM solution of trisodium citrate (Fig. 6).

It can be seen that in the 200–220 nm region, there are multiple absorbing components. The sharp increase near 200 nm is probably the sign of the remaining sulfate ions in the solutions, but aside from that a systematic increase of absorption can be seen in the

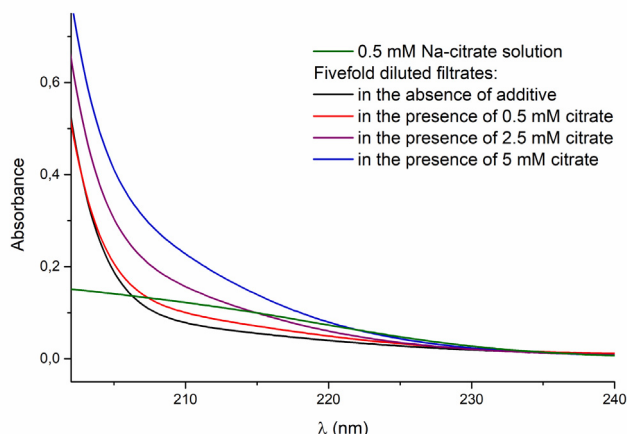


Fig. 6. UV spectra of the fivefold diluted filtrates of the gypsum precipitation reactions (separated from the solids after the end of the reactions) carried out with systematically varied citrate concentration.

200–220 nm region with the increase of the citrate concentration; probably due to the absorption associated with the carboxylate groups of citrate. In these samples, the only component with varying concentration is the citrate, which suggests that the systematic increase in absorption is caused by the increased additive concentration. This implies that the additive stays in the fluid phase, at least partially.

To establish if the solids also contain some of the citrate after the completion of the reaction, the IR spectra of gypsum precipitated in the absence and in the presence of 5 mM trisodium citrate were recorded (Fig. 7).

In both spectra, the characteristic peaks of gypsum can only be seen. The signals around $1100\text{--}1200\text{ cm}^{-1}$ correspond to $\nu_3(\text{SO}_4)$, the wider bands at 2200 cm^{-1} are the combinations of the ν_1 and ν_2 modes of sulfate. The peaks at 1620 and 1680 cm^{-1} correspond to the ν_2 vibration of crystalline water, the sharp peak standing out of the broad band in the region of $3000\text{--}3600\text{ cm}^{-1}$

is the signal of the stretching mode of water [47]. There are not even traces of organic compounds or carboxylic groups present suggesting that the precipitates do not contain detectable amount of citrate.

These results suggest, that practically all of the additive remain in the mother liquor. This could be confirmed by studying the results of the UV measurements in more detail. While the exact concentration cannot be given due to the presence of other interfering absorbing species, the changes should be proportional to the change in the concentration of the additive. Subtracting the spectra of the diluted blank sample from the ones containing citrate, the increase of the absorbance at 209 nm – wavelength of maximum absorption [48] – is linearly proportional to the assumed citrate concentration if all the additive is left in the mother liquor (the equation of the fitted linear is $y = 0.1414x + 0.0075$ and $R^2 = 1$). On the basis of these results we can say that all of the additive is located in the fluid phase after the reactions.

To investigate the effect of increased ionic strength on the efficiency of citrate inhibition, the gypsum was precipitated in the presence of 1 M NaCl . This medium can broadly be considered as model of seawater. In these experiments, the $\text{CaCl}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{NaCl} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ reaction was carried out using 0.1 M initial reactant concentration in the absence and in the presence of 1.5 mM citric acid and trisodium citrate. Since the conductivity of the background electrolyte masks the effect caused by the precipitation reaction, Ca-ISE was used to monitor the reactions. The variation of $[\text{Ca}^{2+}]$ calculated from the results of these measurements are presented in Fig. 8.

When the graphs in Figs. 3 and 8 are compared, it is seen that the precipitation is considerably slower in the presence of 1.0 M NaCl than in its absence. (We note that this is beneficial for the Ca-ISE method, which has slower response time than does conductivity.) The phenomenon is probably caused by the higher solubility of gypsum, and thus smaller supersaturation, caused by the higher ionic strength. The saturation index of gypsum in the absence of further added NaCl is 0.869 while in the systems with higher ionic strength it is only 0.631 (calculated by aqion soft-

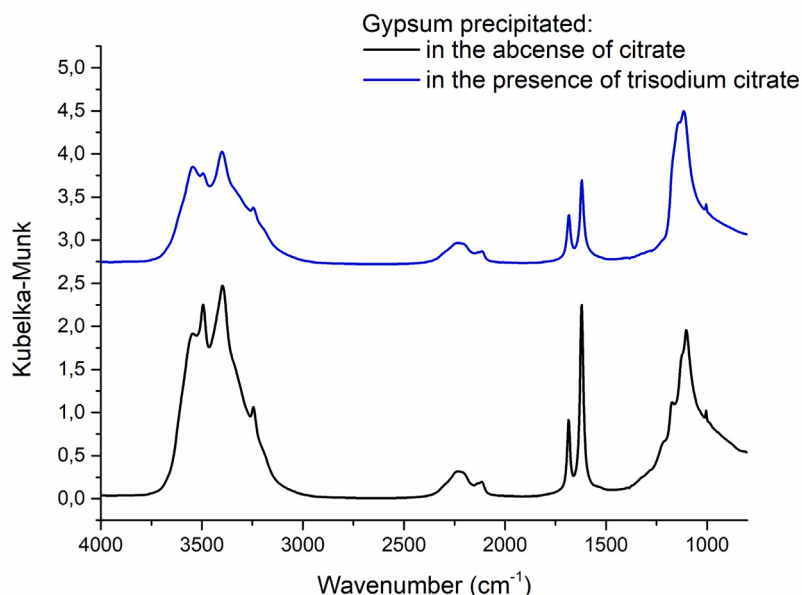


Fig. 7. IR spectra of gypsum precipitated in the absence and in the presence of 5 mM trisodium citrate in the stoichiometric reaction of Na_2SO_4 and CaCl_2 , with 0.1 M reactant concentration.

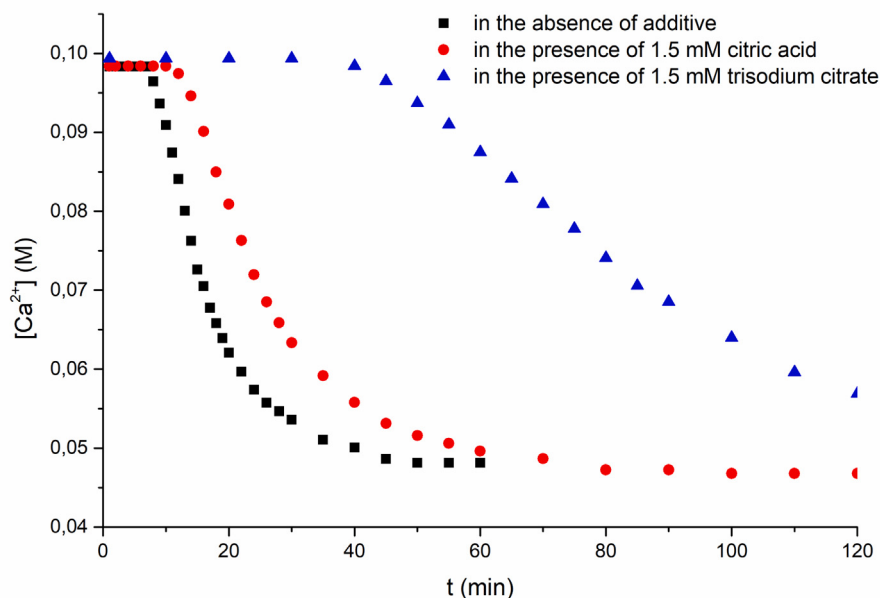


Fig. 8. Variation of $[Ca^{2+}]$ (calculated from the results of Ca-ISE measurements) during the stoichiometric reaction of Na_2SO_4 and $CaCl_2$, with 0.1 M reactant concentration and in the presence of 1.0 M NaCl.

ware). The concentration of calcium at the end of the reaction also confirms this, and it is in agreement with the literature data available on the effect of NaCl on gypsum solubility [49,50]. The difference in inhibiting effect between citric acid and sodium citrate is similar. This was expected, since the pH is the determining factor in these systems. The increased solubility of gypsum also affects the inhibited reactions, in the presence of 1.5 mM citrate, the observed induction period was around 40 min, which is approximately twice as long as the one observed under identical conditions but in the absence of additional NaCl. However, as the supersaturation of these systems is different, direct comparison of them is not possible, we can only say that at a given calcium concentration, the increased ionic strength could increase the induction time by decreasing the supersaturation. These results are very promising for the practical application of citric acid as crystallization inhibitor in high ionic strength environments.

Similarly to the earlier presented experiments, after the reactions were concluded, the precipitated solids were separated from the mother liquor, and were analyzed by powder XRD (Fig. 9).

The changes in the diffractograms show similar tendencies, as the XRD patterns of the samples presented in Fig. 4, but the differences between the individual diffractograms are much smaller. The reflections of the crystal lattices with (0 2 0) and (1 3 0) Miller indices do not stand out as much as in the small ionic strength system, in the absence of the additive. The intensity of these peaks systematically decreases (both in absolute values and in comparison to the other reflections) with the efficiency of the inhibition.

To compare the morphologies of the samples, their SEM images were recorded (Fig. 10). The crystals in every sample seem to be polydisperse, probably due to the breaking of the crystals caused by the intense agitation similarly to the samples presented earlier. The solids precipitated in the absence of additive mainly contain crystals with rod- or needle-like morphologies. In the samples obtained in the presence of citric acid, it can be stated that their main morphology is generally the same as that of the crystals from the additive-free reactions: they form rods and needles. Unlike in the systems without background electrolyte, the crystals are

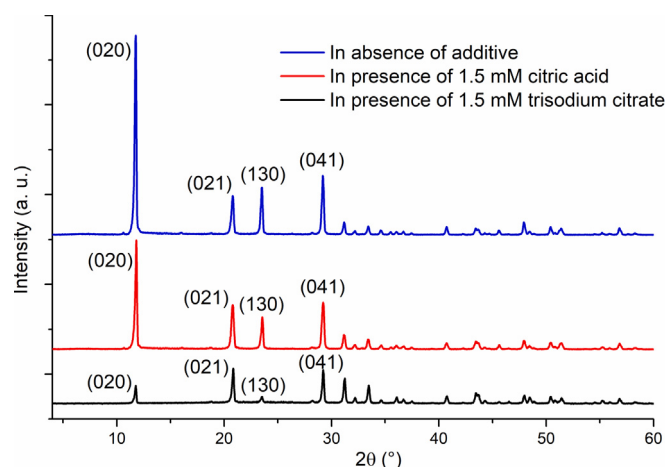


Fig. 9. XRD patterns of the solids precipitated during the stoichiometric reaction of Na_2SO_4 and $CaCl_2$ with 0.1 M reactant concentration, in the presence of 1.0 M additional NaCl and in the presence of various forms of citric acid; the main reflections were identified with the help of the JCPDS database ($CaSO_4 \cdot 2H_2O$: # 21-0816).

mostly short rods, but plate-like forms can also be observed in the samples. NaCl added to the systems in high concentrations increases the overall inhibiting effect, but (relative to the systems without added citrate and NaCl) the morphological changes of the precipitating solids are less dramatic in the presence than in the absence of added electrolyte. As we can see on Fig. 8 the presence of citrate ions slows down both the nucleation and crystal growth processes, but the formed crystals have slightly different morphologies, implying that chloride ions change the inhibition mechanism of citrate.

According to the results of our measurements, citric acid (in citrate form) can act successfully as an inhibitor of gypsum precipitation even under hypersaline conditions. The higher ionic strength of the processes involving seawater is beneficial even

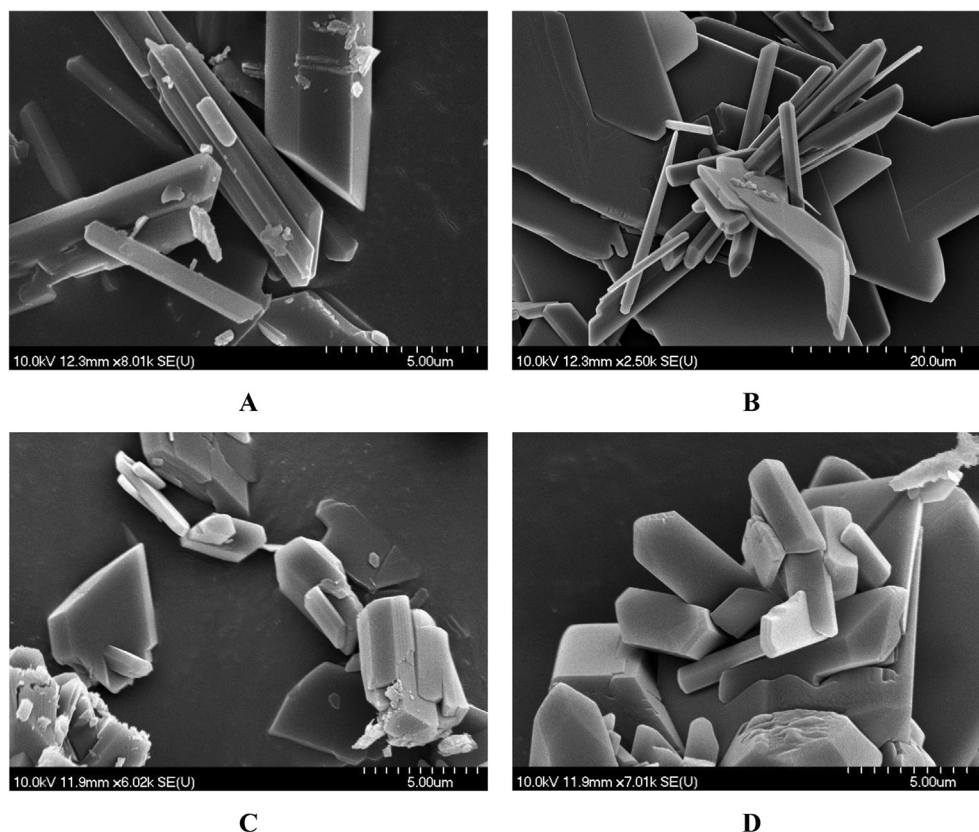


Fig. 10. SEM images of gypsum precipitated during the stoichiometric reaction of Na_2SO_4 and CaCl_2 , with 0.1 M reactant concentration in the presence of 1 M additional NaCl, A: in the absence of additive, B: in the presence of 1.5 mM citric acid and C, D: in the presence of 1.5 mM trisodium citrate.

for practical application, since the solubility of gypsum is higher in these systems, and thus, the efficiency of the inhibition is higher as well.

4. Conclusions

The effects of citric acid on the precipitation of gypsum from highly supersaturated solutions was investigated in the stoichiometric reaction between Na_2SO_4 and CaCl_2 at various pH-s and in the presence and absence of added electrolyte (NaCl). The efficiency of the crystallization inhibition of gypsum by citrate sharply drops under pH 4 due to the protonation of the carboxylic groups of citrate ions, while between pH 5 and 10 the reaction kinetics did not change significantly. The increase of the additive concentration does not increase the induction time proportionally, the efficiency of inhibition levels off at ca. 3 mM citrate concentration. This is most probably due to the saturation of the surfaces of the particles (preliminary phases) smaller than the critical nucleus size, to which the additive can be bound.

The effects of citrate on the structure of the precipitate (the only identifiable solid was gypsum) were also investigated. It was observed in the XRD patterns of the samples that the intensity of the most intense peaks decreased (both absolutely and compared to the other reflections) with the increasing inhibiting effect. This implies that the morphology of the crystal also changed, the rod- or needle-like shaped crystals formed in the absence of inhibitor changed to plate-like shapes in the presence of the citrate ions. The latter was further confirmed with SEM measurements.

From the UV spectra of the filtrate of the reaction mixtures after the completion of the reactions and the IR spectra of the filtered gypsum, it was concluded that the inhibitor remained in solution,

and that the citrate was not incorporated in the solid in detectable amounts.

To test the inhibiting efficiency of citric acid and citrate in processes involving solution mimicking seawater, the precipitation of gypsum was carried out in the presence of 1 M NaCl as background electrolyte. Since the solubility of gypsum is increased at higher ionic strength, the reaction rate was found to be slower, hence the inhibiting efficiency of the same amount of citrate ion is much better. Studying the solids precipitating from these reactions, the differences found were not as pronounced as those observed at low ionic strength systems. The morphology of the solids also changed, however beside the sporadic appearance of platelets, the majority of the crystals formed short rods, implying that the presence of large amounts of NaCl alters the mechanism of citrate inhibition.

CRediT authorship contribution statement

Szilveszter Ziegenheim: Conceptualization, Methodology, Investigation, Writing - original draft. **Márton Szabados:** Formal analysis, Investigation. **Zoltán Kónya:** Resources. **Ákos Kukovecz:** Resources. **István Pálínkó:** Supervision, Project administration, Funding acquisition, Writing - review & editing. **Pál Sipos:** Supervision, Project administration, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] O.J. Schierholtz, *Can. J. Chem.* 36 (1958) 1057–1063.
- [2] E.R. McCartney, A.E. Alexander, *J. Colloid Sci.* 13 (1958) 383–396.
- [3] W.-Y. Shih, K. Albrecht, J. Glater, Y. Cohen, *Desalination* 169 (2004) 213–221.
- [4] S.T. Liu, G.H. Nancollas, *J. Colloid Interfaces Sci.* 52 (1975) 593–601.
- [5] P.G. Klepetsanis, P.G. Koutsoukos, *J. Cryst. Growth* 193 (1998) 156–163.
- [6] M. Prisciandaro, E. Olivieri, A. Lancia, D. Musmarra, *Ind. Eng. Chem. Res.* 45 (2006) 2070–2076.
- [7] M. Prisciandaro, E. Olivieri, A. Lancia, D. Musmarra, *Ind. Eng. Chem. Res.* 48 (2009) 10877–10883.
- [8] E. Akyol, M. Öner, E. Barouda, K.D. Demadis, *Cryst. Growth Des.* 9 (2009) 5145–5154.
- [9] M. Prisciandaro, E. Olivieri, A. Lancia, D. Musmarra, *Ind. Eng. Chem. Res.* 51 (2012) 12844–12851.
- [10] H. El-Shall, M.M. Rashad, E.A. Abdel-Aal, *Cryst. Res. Technol.* 37 (2002) 1264–1273.
- [11] T.A. Hoang, A.H. Ming, A.L. Rohl, *Aust. J. Chem.* 62 (2009) 927–933.
- [12] M.P.C. Weijnen, G.M. van Rosmalen, *Desalination* 54 (1985) 239–261.
- [13] M.G. Lioliou, C.A. Paraskeva, P.G. Koutsoukos, A.C. Payatakes, *J. Colloid Interfaces Sci.* 303 (2006) 164–170.
- [14] X. Xue, C. Fu, N. Li, F. Zheng, W. Yang, X. Yang, *Water Sci. Technol.* 66 (2012) 193–200.
- [15] Z. Amjad, *Desalin. Water Treat.* 51 (2013) 4709–4718.
- [16] Z. Amjad, P.G. Koutsoukos, *Desalination* 335 (2014) 55–63.
- [17] T. Feldmann, G.P. Demopoulos, *J. Chem. Technol. Biotechnol.* 89 (2014) 1523–1533.
- [18] K. Popov, G. Rudakova, V. Larchenko, M. Tusheva, S. Kamagurov, J. Dikareva, N. Kovaleva, *Adv. Mater. Sci. Eng.*, 2016.
- [19] T. Rabizadeh, D.J. Morgan, C.L. Peacock, L.G. Benning, *Ind. Eng. Chem. Res.* 58 (2019) 1561–1569.
- [20] J. Benecke, J. Rozova, M. Ernst, *Sep. Purif. Technol.* 198 (2018) 68–78.
- [21] M.H.H. Mahmoud, M.M. Rashad, I.A. Ibrahim, E.A. Abdel-Aal, *J. Colloids Interfaces Sci.* 270 (2004) 99–105.
- [22] S.K. Hamdonaa, O. Al Hadad, *Desalination* 228 (2008) 277–286.
- [23] E. Badens, S. Veesler, R. Boistelle, *J. Cryst. Growth* 198 (199) (1999) 704–709.
- [24] T. Rabizadeh, C.L. Peacock, L.G. Benning, *Miner. Mag.* 78 (2014) 1465–1472.
- [25] C. Vellmer, B. Middendorf, N.B. Singh, *J. Therm. Anal. Calorim.* 86 (2006) 721–726.
- [26] M. Prisciandaro, A. Lancia, D. Musmarra, *Eng. Chem. Res.* 42 (2003) 6647–6652.
- [27] M. Prisciandaro, A. Santucci, A. Lancia, D. Musmarra, *Can. J. Chem. Eng.* 83 (2005) 586–592.
- [28] S. Titiz-Sargut, P. Sayan, A. Avci, *Cryst. Res. Technol.* 42 (2007) 119–126.
- [29] S. Titiz-Sargut, P. Sayan, B. Kiran, *Chem. Eng. Technol.* 33 (2010) 804–811.
- [30] J. Qu, J. Peng, B. Li, *Adv. Mat. Res.* 250 (2011) 321–326.
- [31] M.M. Rashad, M.H.H. Mahmoud, I.A. Ibrahim, E.A. Abdel-Aal, *Cryst. Res. Technol.* 40 (2005) 741–747.
- [32] L. Lv, R. Gao, J. Yang, Z. Shen, Y. Zhou, J. Lu, *Chem. Ind. Chem. Eng. Q.* 23 (2017) 161–167.
- [33] A. Ersen, A. Smith, T. Chotard, *J. Mater. Sci.* 41 (2006) 7210–7217.
- [34] E. Najafi Kani, M. Nejan, A. Allahverdi, *Iran. J. Mater. Sci. Eng.* 13 (2016) 61–70.
- [35] Y. Deng, J. Luo, D. Zai, L. Xuan, Z. Han, C. Dai, H. Xu, M. Feng, G. He, *Holzforchung* 62 (2008) 368–371.
- [36] S. Raharjo, S. Muryanto, J. Jamari, A.P. Bayuseno, *Orient. J. Chem.* 32 (2016) 3145–3154.
- [37] M.E. Tadros, I. Mayes, *J. Colloid Interfaces Sci.* 72 (1979) 245–254.
- [38] A. Al-Sabbagh, J. Widua, H. Offermann, *Chem. Eng. Comm.* 154 (1996) 133–145.
- [39] W. Chen, W. Zhao, Y. Wu, Y. Wang, B. Zhang, F. Li, Q. Chen, Z. Qi, Z. Xu, *Cryst. Eng. Comm.* 20 (2018) 3581–3589.
- [40] E. van der Voort, P. Hartman, *J. Cryst. Growth* 112 (1991) 445–450.
- [41] Sz. Ziegenheim, G. Peintler, I. Pálkó, P. Sipos, *React. Kinet. Mech. Cat.* 131 (2020) 75–88.
- [42] D.R. Lide (Ed.), *CRC Handbook of Chemistry and Physics: A Ready Reference Book of Chemical and Physical Data*, 84th ed., CRC Press, 2002.
- [43] J. Schubert, A. Lindenbaum, *Nature* 166 (1950) 913–914.
- [44] T.M. Stawski, A.E.S. van Driessche, M. Ossorio, J.D. Rodríguez-Blanco, R. Besselink, L.G. Benning, *Nat. Commun.* 7 (2016) 11177.
- [45] M. Ossorio, T.M. Stawski, J.D. Rodríguez-Blanco, M. Sleutel, J.M. García-Ruiz, L. G. Benning, A.E.S. van Driessche, *Minerals* 7 (2017) 140.
- [46] L. Nicoleau, A.E.S. van Driessche, M. Kellermeier, *Cement Concr. Res.* 124 (2019) 105837.
- [47] J. Bensted, S. Prakash, *Nature* 219 (1968) 60–61.
- [48] S. Krukowski, M. Karasiewicz, W. Kolodziejewski, *J. Food Drug Anal.* 25 (2017) 717–722.
- [49] F.K. Cameron, *J. Phys. Chem.* 5 (1901) 556–576.
- [50] E. Bock, *Can. J. Chem.* 39 (1961) 1746–1751.